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(71) Applicant: GENERAL ELECTRIC COMPANY [US/US]; 1 River Road, Schenectady, NY 12345 (US).

(72) Inventor: SUN, Xiao-Dong; 1455 Dorwaldt Boulevard, Schenectady, NY 12309 (US).

(74) Agents: SNYDER, Bernard et al.; General Electric Company, 3135 Easton Turnpike W3C, Fairfield, CT 06431 (US).

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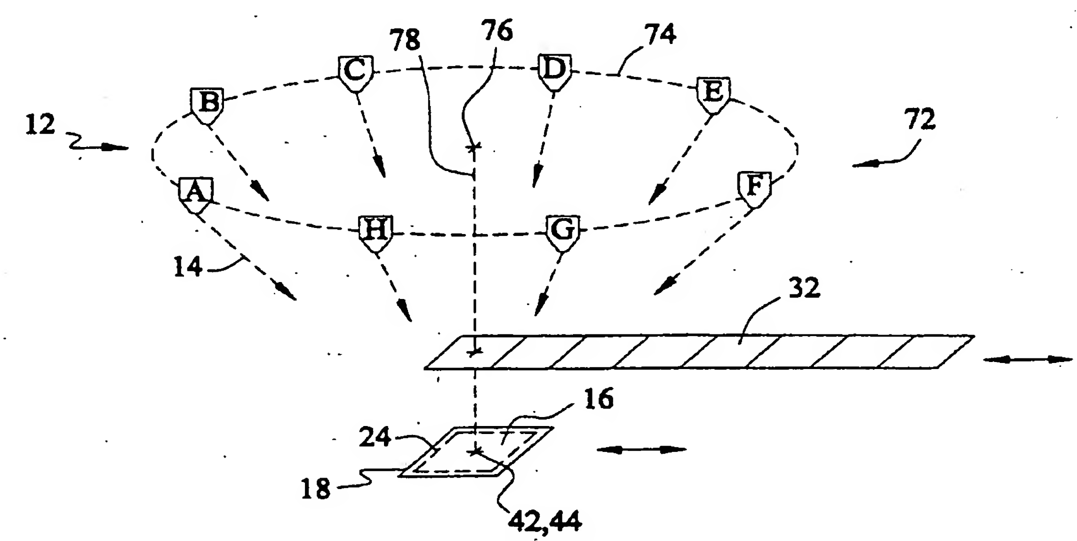
(54) Title: COMBINATORIAL COATING SYSTEMS AND METHODS



(57) Abstract: Systems and method for high throughput fabrication and analysis of an array of coated materials. The methods include selectively delivering at least one of a plurality of materials (14) to the surface (16) of a substrate (18) having a plurality of predefined regions (22) to form a predefined coating (30) on each of the regions. In the selective delivery of the materials, each of the plurality of materials is positioned for simultaneous delivery to the substrate. The systems(10) include a substrate (18) having a surface (16) with a plurality of predefined regions (22), where a plurality of materials (14) are provided for coating the substrate. A delivery mechanism (12) associated with the plurality of materials is positioned to simultaneously deliver each of the plurality of materials onto the surface of the substrate. Further, a controller (26) is utilized to control the delivery mechanism to selectively deliver each of the plurality of materials such that each of the plurality of the predefined regions of the substrate has a predefined coating (30).

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

COMBINATORIAL COATING SYSTEMS AND METHODS

BACKGROUND OF THE INVENTION

This disclosure relates generally to methods and apparatus for generating and screening coating libraries, and more particularly, to methods and systems for the parallel deposition of layers of materials onto a substrate to form a coating library.

Coatings are widely used in industry to enhance the functionality and add-on value of bulk materials. There are generally two types of functional coating materials: inorganic and organic coatings. Inorganic coatings have been used in both the semiconductor industry, for example in various thin film integrated circuit devices, as well as in conventional industry, such as thermal barrier coatings for steam turbines and aircraft engine airfoils. Organic coatings are also widely used in many industrial protective/decorative applications, such as in automobile top clear coatings, paints, etc. Other types of coatings include, for example, protective and anticorrosive coatings, adhesive and release coatings, environmental barrier coatings, electric conductive/optic transparent coatings, scratch resistance hard coatings, etc. Discovery of an advanced coating formula promises huge value for a manufacturer.

The development of generic tools to accelerate the discovery process for various coating systems may be of even higher value, however, as the search and optimization of advanced coatings is more of an art than a science. The power of theoretical guidance in the search and optimize advanced coatings is limited, largely because of the complexity of a typical coating system and multiplicity of quality requirements that need to be met. Typically, industrial coating formulations have to meet multiple functional requirements, and multiple compatible functional groups or blends are necessary to obtain a balanced formulation. In addition, the properties of a coating system depend not only on the formulation/composition, but also on the processing conditions and the coating application method. For example, the degree of thickness uniformity and surface roughness, which depends on the application method

and processing of a coating, are important in the quality and reproducibility of the coating. Further, different processing conditions, including exposure to ultra-violet(UV)/electron curing; varying temperature/pressure, and the sequence of application of each layer of multiple layer coatings, are highly important factors in determining the structure/composition of the final coating. Additionally, the structure/composition of the final coating impacts the functionality of the coating. Thus, because of the multitude of variables, most of the usable industrial coating systems developed to date have been a result of serendipitous trial-and-error experimental processes.

BRIEF SUMMARY OF THE INVENTION

Therefore, there is a need for an approach that accelerates the rate at which functional coatings are generated and studied for various manufacturing applications. Thus, the present invention provides systems and methods for high throughput fabrication and analysis of an array of coated materials.

A system of one embodiment for making an array of coated materials includes a substrate having a surface with a plurality of predefined regions, where a plurality of materials are provided for coating the substrate. A delivery mechanism associated with the plurality of materials is positioned to simultaneously deliver each of the plurality of materials onto the surface of the substrate. Further, a controller is utilized to control the delivery mechanism to selectively deliver each of the plurality of materials such that each of the plurality of predefined regions of the substrate has a predefined coating.

A method of one embodiment for making an array of coated materials includes selectively delivering at least one of a plurality of materials to the surface of a substrate having a plurality of predefined regions to form a predefined coating on each of the regions. In the selective delivery of the materials, each of the plurality of materials is positioned for simultaneous delivery to the substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic diagram of a system for making an array of coating materials;

Fig. 2 is a schematic diagram of a coating library formed from the system of Fig. 1;

Fig. 3 is a schematic diagram of an envelope of a vaporized material being delivered from a delivery mechanism source to the surface of a substrate within a delivery area;

Fig. 4 is a graph of a thickness profile distributed across a dimension of a delivery area from a normal, focused set up of the delivery mechanism;

Fig. 5 is a graph of a thickness profile distributed across a dimension of a delivery area from an angled, focused set up of the delivery mechanism source;

Fig. 6 is a graph of a thickness profile distributed across a dimension of a delivery area from a normal, off-focus set up of the delivery mechanism source;

Fig. 7 is a graph of a thickness profile distributed across a dimension of a delivery area from an angled, off-focus set up of the delivery mechanism source;

Fig. 8 is a side view of one embodiment of a combinatorial coating system having two opposing delivery sources;

Fig. 9 is a top view of a coating library formed from the system of Fig. 8;

Fig. 10 is a perspective view of one embodiment of a ternary combinatorial coating system;

Fig. 11 is a top view of a coating library formed from the system of Fig. 10;

Fig. 12 is a schematic diagram of another embodiment of a combinatorial coating system;

Fig. 13 is a top view of a mask having a plurality of patterns, as may be utilized in the system of Fig. 12;

Fig. 14 is a top view of a coating library formed using the mask of Fig. 13 in the system of Fig. 12; and

Fig. 15 is a side view showing the cross-section of one embodiment of a vapor deposition combinatorial coating system.

DETAILED DESCRIPTION OF THE INVENTION

Referring to Figs. 1 and 2, a system 10 for making an array of coating materials that form a coating library includes a delivery mechanism 12 delivering one or a combination of a plurality of materials 14 to a surface 16 of a substrate 18 to form a coating 20. The substrate surface 16 has a plurality of predefined regions 22 that are positioned within a delivery area 24, which is preferably at a fixed location within the system 10. The delivery mechanism 12 and/or the plurality of materials 14 are positioned to simultaneously deliver, or deliver in parallel, each of the plurality of materials to the delivery area 24. A controller 26 controls the selection, quantity and sequence of delivery of each of the plurality of materials 14 such that the composition of the coating 20 may vary between each of the regions 22 on the substrate surface 16 to form a coating library 28. As such, each of the plurality of predefined regions 22 is coated with one of a plurality of predefined coatings 30. The plurality of predefined coatings 30 include: a single layer coating of one of the plurality of materials 14; a single layer coating of a combination of the plurality of materials; a multiple layer coating, where each layer is one of the plurality of materials; and a multiple layer coating, where each layer is a combination of the plurality of materials. Additionally, the system 10 may include a mask 32 in communication with the controller 26 to permit delivery of the materials 14 to different combinations of the plurality of predefined regions 22 form the plurality of predefined coatings 30. The system 10 may also include a curing source 34 for curing the plurality of materials 14, either as they are being delivered to the substrate 18 or once they have been deposited on the substrate. Further, the system 10 may include a testing device 36 to perform

analytical tests on the coated substrate or coating library 28, to determine the properties of each of the plurality of predefined coatings 30. The mask 32 may be secured by a mounting device 35, which optionally may movably position the mask within the system 10. Similarly, the substrate 18 may be secured by a holding device 37, which optionally may movably position the substrate within the system 10. Thus, the present invention provides a system and method for manufacturing and testing a coating library having an array of coatings established from a plurality of materials simultaneously focused, or focused in parallel, on a substrate.

The delivery mechanism 12 is configured such that each of the plurality of materials 14 may be simultaneously delivered, or delivered in parallel, to the delivery area 24 from a variety of angles. As such, the delivery mechanism 12 is positioned or focused so that at least a portion of the delivered material reaches the delivery area 24, as is discussed in more detail below. The delivery mechanism 12 may be a single device, or it may be a plurality of individual devices each corresponding to one of the plurality of materials 14. The position of each of the one or more delivery mechanisms 12 is preferably fixed within the system 10 relative to the delivery area 24 and relative to the other delivery mechanisms. Preferably, the delivery mechanism 12 projects each of the plurality of materials 14 to the delivery area 24 in a vaporized or atomized form. Suitable examples of a delivery mechanism 12 include: a spray nozzle or gun of any type, such as ultrasonic, air, thermal, airless guns, such as those using hydraulic force; microwave or radio frequency ("RF") delivery mechanisms; an ink jet print head; a vapor deposition device, including sputtering, thermal/electron/laser evaporation, chemical vapor deposition (CVD), molecular beam epitaxy, plasma spray; and ion beam deposition.

The plurality of materials 14 include inorganic materials and organic materials in various states, such as solid, liquid, gaseous and vaporized/atomized materials. Suitable examples of inorganic coatings include metals, alloys, ceramics, oxides, nitrides, and sulfides. Suitable examples of organic coatings include polymeric, oligomeric and small molecules, where small molecules are individual monomers that react to form a coating. The polymeric materials include, but are not limited to, polycarbonates, acrylics, silicones, cellulose esters, polyesters, alkyds, polyurethanes,

and vinyl polymers and alike. Preferably, the plurality of organic materials include organic polymeric materials, such as "architectural" materials derived from organic materials having protective or decorative functionality, especially including thermoplastic or thermosetting polymers. Preferably, the plurality of inorganic materials include oxides. Further, the plurality of materials 14 preferably can be vaporized or atomized, individually or in combination, and directed to or deposited on a substrate, where the vaporized/atomized material coalesces and forms a continuous coating if a sufficient amount of the material is delivered to the substrate. Additionally, the material or combination of materials may form a coating having a plurality of layers, where the coating may be a multi-functional coating having an overall function dictated by a predefined functional role of each layer. The materials may be combined such that multiple organic materials, or multiple inorganic materials, or a combination of organic and inorganic are combined into a coating. Additionally, by providing these various combinations of materials, the interaction and compatibility of various combinations of materials may be determined.

The coating 20 is a material or a combination of materials deposited on the substrate 18. These materials may remain as separate homogenous materials, or they may react, interact, diffuse, mix or otherwise combine to form a new homogeneous material, a mixture, a composite or a blend. As mentioned above, the coating 20 may include a single layer or multiple layers. In general, coating 20 has a lateral measure, i.e. a measured length across the surface of the substrate, much greater than a thickness, i.e. a measure of the coating normal to the surface of the substrate. Preferably, each layer is a thin film layer. The coating 20 may vary in composition, optionally in a continuous manner, from one predefined region 22 to another to thereby form an array of coatings that define the plurality of predefined coatings 30 of the coating library 28. Each of the array of coatings are distinguishable from each other based on their location. Further, each of the array of coatings may be processed under the same conditions and analyzed to determine their performance relative to functional or useful properties, and then compared with each other to determine their relative utility.

Each of the plurality of predefined regions 22 is a fixed area on the substrate 18 for receiving one or a combination of the plurality of materials 14 to form a single or multiple layer coating. Each of the predefined regions 22 may have any shape sufficient for receiving and analyzing the coating deposited thereon, such as rectangular, linear, arcuate, circular, elliptical, combinations thereof, etc. Each predefined region 22 typically has an area in the range of about 0.01 mm^2 to about 100 cm^2, preferably in the range of about 1 mm^2 to about 1 cm^2, and more preferably in the range of about 10 mm^2 to about 50 mm^2. Other areas may be utilized, and the area of each predefined region 22 may be determined by the capability of deposition and analytical devices and by a preferred density of the coating library.

The substrate 18 is a rigid or semi-rigid material suitable for receiving and supporting at least one of the plurality of materials 14. The substrate 18 has at least one substantially flat surface 16 that includes the plurality of predefined regions 22. This substantially flat surface, however, may have raised portions to physically separate each of the plurality of predefined regions 22. The substrate 18 may be of any size and shape, but preferably is in a disk shape, plate shape, or elongated shape, such as in a tape or roll. The substantially flat surface 16 of the substrate 18, corresponding to the delivery area 24, typically has an area in the range of about 1 mm^2 to about 1 m^2, preferably in the range of about 50 mm^2 to about 750 cm^2, and more preferably in the range of about 1 cm^2 to about 500 cm^2.

The substrate 18 may be secured within the system 10 and positioned in the delivery area 24 by the holding device 37. The holding device 37 may movably position the substrate 18. For example, for a substrate 18 in the form of an elongated tape, the holding device 37 may include a tape pay-out device and a tape take-up device that are both rotatable and that support the tape, possibly in combination with rollers, in the delivery area 24. In another example, the holding device 37 may be a plate on which the substrate is placed and secured, where the plate is connected to a motor or other actuator-type device that controls the position of the plate relative to the delivery area 24. As such, the controller 26 may control the movement of the holding device 37 to control the predefined regions 22 onto which the materials 14 are delivered. For example, the controller 26 may move the holding device 37 such that

predetermined ones of the plurality of predefined regions 22 are outside of the delivery area 24 and therefore do not receive one or more of the materials 14.

The delivery area 24 is an area at a fixed position within the system 10. The delivery area 24 may be of any shape or size and typically, but not necessarily, substantially corresponds in shape and size to the plurality of predefined regions 22 on the surface 16 of the substrate 18. However, the plurality of predefined regions 22 may be much larger or much smaller than the delivery area 24. The fixed positioning of the delivery area 24 provides a known, constant locale for the system 10 to deliver the plurality of materials 14 and the surface 16 of the substrate 18.

The controller 26 is a computer system having inputs, outputs, a memory and a processor for receiving, sending, storing and processing signals and data to operate, monitor, record and otherwise functionally control the operation of the system 10. The controller 26 includes a computer system having an interface board for integrating all of the components of the system and a motion controller for controlling the movements of the mask 32 and substrate 18. The controller 26 may include a keyboard for inputting data and commands, a video display for displaying information, and a printer for printing information. The controller 26 may include software, hardware, firmware, and other similar components and circuitry for operating the system 10. The controller 26 may be a single device, or it may be a plurality of devices working in concert. The controller 26 is preferably in communication with all of the other components of the system 10, including the delivery mechanism 12, the plurality of materials 14, the substrate 18, the mask 32, the curing source 34, the testing device 36, the mounting device 35 and the holding device 37, to coordinate the operations of the system. For example, the controller controls the delivery of the materials to the substrate, recording the exact combination of materials that make up the coating at each predefined region. By controlling the delivery, the controller may control one or more of the material volume, the combination of materials, the projective power, the coating speed, the projective angle, the spacing between the delivery mechanism and the substrate, the masking, etc. Further, the controller 26 controls, synchronizes, combines and records the

delivery and curing of the delivered materials, the testing of the coating library, and the analysis of the test results.

The mask 32 is a material having one or more patterns of open areas and blocked areas, where the open areas allow delivery of the plurality of materials 14 to the substrate 18 and the blocked areas block the delivery. The pattern may be in any shape. The mask 32 is utilized to define the spatial variation of materials in the coating library 28. In a binary masking system, for example, the mask includes a plurality of patterns that are sequentially arranged to allow delivery to alternating half areas on the substrate 18, as will be described below in more detail. The mask 32 may be positioned anywhere in between the plurality of materials 14 and the substrate 18, including positioned directly on top of and in contact with the substrate, along the line of delivery of the materials. By increasing the spacing between the mask 32 and the substrate 18, an effect called "shadowing" is produced which may be undesirable in some instances. In shadowing, the pattern of material delivered to the substrate is proportional to the pattern of the mask, but larger, as the spacing between the mask and the substrate allows the delivered pattern to expand until it reaches the substrate. The mask 32 may be formed of a rigid or semi-rigid material, or the mask may be a chemical formed on the surface of the substrate. Preferably, the material of the mask insures that the mask is as flat as possible and resists bending and/or folding. Suitable examples of mask materials include: silicon, silicon oxide and glass for rigid or relatively non-bendable materials; plastics, metals and alloys for semi-rigid or relatively bendable materials in the form of sheets, films or foils; and lithographic-polyacrylate ("PMMA") and other chemical materials that form negative and positive chemical masks.

The mask 32 may be secured within the system 10 and positioned relative to the delivery area 24 by the mounting device 35. The mounting device 35 may movably position the mask 32. For example, for a mask 32 in the form of an elongated semi-rigid material having a plurality of patterns, the mounting device 35 may include a tape pay-out device and a tape take-up device that are both rotatable and that support the tape, possibly in combination with rollers, relative to the delivery area 24. In another example, for a mask 32 in the form of a rigid material, the

mounting device 35 may be a platform or other supporting structure connected to a motor or other actuator-type device that controls the position of the platform and mask relative to the delivery area 24. This allows one pattern or a number of patterns to be utilized to mask different predefined regions 22 on the substrate 18 by movement of the mask 32. As such, the controller 26 may control the movement of the mounting device 35 to control the predefined regions 22 onto which the materials 14 are delivered.

The curing source 34 is a device in communication with each of the plurality of materials 14 to cause a reaction or a solvent evaporation with one or a combination of the materials. For example, the reaction may be a polymerization, a cross-linking reaction, a small molecule reaction, an inorganic phase reaction, and other similar reactions appropriate for the delivered material(s). Suitable examples of a curing source 34 include a heating device in communication with the substrate 18, a radiation device in communication with the delivered materials or the deposited materials, a microwave device, a plasma device and combinations thereof.

The testing device 36 is a system for analyzing the performance of each of the plurality of predefined coatings 30 on the substrate 18. The testing device 36 subjects the entire coating library 28 to the same conditions in order to determine the relative performance of each one of the predefined coatings 30. The testing device 36 is in communication with the controller 26 in order to compile and analyze the test data. Suitable examples of a testing device 36 include a thickness profiler, a surface analyzer, an ultra violet ("UV") absorbance tester, a scratch resistance tester, a permeability tester, and other similar devices that test architectural, protective, decorative and other functional features of a coating.

Referring to Fig. 3, a source 38 of the delivery of the materials from the delivery mechanism 12 delivers one of the plurality of materials 14 in a vaporized or atomized state within an envelope 40 that preferably encompasses the delivery area 24 in order to obtain coating coverage over the entire delivery area. The source 12 is the point of exit of the material from the delivery mechanism. For example, the source 12 may be the nozzle on a spray gun. It may be desired in some cases,

however, not to have coating coverage over the entire delivery area 24. For example, the envelope 40 may only encompass a portion of the delivery area 24 when a portion of the predetermined regions 22 of the substrate 18 are not to be coated and a mask 32 is not being used to prevent delivery of the material to those regions. The envelope 40 may be of any convenient shape, including: conical with various cross-sections such as round, elliptical and rectangular; semi-conical with various cross-sections; and a thin line shape. The shape of the envelope 40 may be dictated by the shape of the delivery area 24, the shape of the surface 16 of the substrate 18, the delivery mechanism 12, the desired composition of each of the plurality of predefined coatings 30, the shape and number of the predetermined regions 22, the number of sources 38, the number of materials 14 being delivered to the substrate 18, and similar factors. The shape of the envelope 40 may be controlled by the shape of a nozzle on the delivery mechanism 12, by an air shroud associated with the delivery mechanism, or by other shape-defining structures or devices associated with the delivery mechanism.

Referring to Figs. 3 and 4, in a normal focused set up 41, the source 38 has a point of focus 42 for delivering the material 14 coinciding with a center point 44 of the delivery area 24. The source 38 is positioned to direct the material 14 along a delivery angle having a centerline 46 substantially perpendicular to the surface of the delivery area 24 at the center point 44. Referring to Fig. 4, the cross-sectional thickness profile 48 along one of the dimensions 50 (such as the lateral dimension of Fig. 3) of the delivery area 24 of a coating delivered from the set-up of Fig. 3, with the delivery angle α substantially perpendicular to the plane 49 of the delivery area, typically has a 2-dimensional substantially Gaussian or normal distribution. The thickness profile 48 therefore has an apex 52 coinciding with the centerline 46 above the center point 44, with two equal, mirror-image tails 54 on each side of the centerline. Further, the source 38 is positioned at a vertical spacing 60 relative to the plane 49 of the delivery area 24 (Fig. 3). The vertical spacing 60 affects the total width 51 of the thickness profile 48 and thereby the thickness of the coating at any given point along the thickness profile distribution. Thus, in this case, the thickness profile 48 is centered within the dimension 50 of the delivery area 24, the thickness

being largest at the apex 52 and gradually reducing in all directions from the centerline 46.

Referring to Fig. 5, in an angled focused set up 55, the source 38 has the point of focus 42 for delivering the material 14 coinciding with the center point 44 of the delivery area 24, however, the source is positioned such that the centerline 46 of the material is at a delivery angle α between about 0 degrees and about 90 degrees relative to the plane 49 of the delivery area. Further, because of the angled but focused delivery, the source 38 is located at a horizontal spacing distance 53 from the center point 44. The horizontal spacing distance 53 is a distance in the plane of the source 38 parallel to the plane 49 of the delivery area and spaced away from the normal focused set up position. The horizontal spacing distance 53, vertical spacing distance 60, and delivery angle α are all mathematically interrelated and may be varied to position the thickness profile 48 within the delivery area 24. In this embodiment, the thickness profile 48 has a distorted Gaussian distribution with an inclined tail 56 closer to the source 38 and an elongated tail end 58 trailing away from the source. Within the elongated tail 58 is typically a region where the thickness profile 48 varies substantially linearly with the length along the dimension 50. Thus, in this case, the thickness profile 48 is distorted within the dimension 50 of the delivery area 24, the thickness being largest toward the end of the dimension having the inclined tail 56 and reducing in thickness from the apex 52 toward the edge of the dimension corresponding to the elongated tail 58.

Referring to Fig. 6, in an normal off-focus set up 57, the source 38 has the point of focus 42 for delivering the material 14 positioned at an offset distance 59 in the plane of the delivery area 24 along the dimension 50 from the center point 44. In this case, where the centerline 46 is at a delivery angle α substantially perpendicular to the plane 49 of the delivery area 24, the offset distance 59 is substantially equivalent to the horizontal spacing of the source 38 from the normal focused set up position (Fig. 4). Also, note that the point of focus for a delivery mechanism may be positioned within the delivery area or outside of the delivery area. Thus, in this case, the thickness profile 48 is offset within the dimension 50 of the delivery area 24, the

thickness being largest at the offset position of the apex 52 and gradually reducing in all directions from the centerline 46.

Referring to Fig. 7, in an angled off-focus set up 61, the source 38 has the point of focus 42 for delivering the material 14 positioned at the offset distance 59 along the dimension 50 from the center point 44, where the centerline 46 is at a delivery angle α between about 0 degrees and about 90 degrees relative to the plane 49 of the delivery area 24. In this case, because of the delivery angle α and off-focus point of focus 42, the horizontal spacing 53 of the source 38 from the normal focused delivery point is greater than the offset distance 59 of the point of focus to the center point 44. Thus, in this case, the thickness profile 48 is even more distorted within the dimension 50 of the delivery area 24 than the set up of Fig. 5.

In each of the set ups of Figs. 4-7, the flatness of the thickness profile 48 within the delivery area 24 will vary depending on the vertical spacing 60 between the source 38, where the flatness will increase with increased spacing. Further, the flatness of the thickness profile 48 will vary within the delivery area 24 depending on the delivery angle α, horizontal spacing 53, and offset distance 59, where the smaller the angle and greater the horizontal spacing and offset distance will increase the flatness. For example, referring to Fig. 4, the thickness profile 48 may be substantially flat in the dimension 50 of the delivery area 24 with the proper combination of delivery angle, horizontal spacing and offset distance. With closer spacing, however, the thickness profile 48 in the dimension 50 of the delivery area 24 may gradually change from a largest thickness at the apex 52 to a smallest thickness at the edges of the dimension of the delivery area. Preferably, a coating library having a substantially constant thickness is desired so that the thickness variable can be ruled out of the analysis of the plurality of predefined coatings 30 associated with each predefined region 22 in order to focus the study on the effect of the coating composition. In operation, a substantially constant thickness coating library is achieved by calibrating each delivery mechanism such that a linear thickness profile is distributed across the delivery area. When multiple delivery mechanisms are utilized, preferably the same portion of the thickness profile is positioned within the

delivery area for each delivery mechanism. Therefore, the present invention allows the manufacture of coating libraries having virtually infinite variations in compositions, layers and thicknesses of coating materials within the plurality of predefined regions 30 of the substrate 18 by varying the vertical spacing 60, the delivery angle α and the offset distance 59, for each source 38 of each of the plurality of materials 14.

Referring to Figs. 8 and 9, in one embodiment of a combinatorial coating system 62, a continuously varying coating library 64 is formed on the substrate 18 by the simultaneous deposition of at least two (A and B) of the plurality of materials 14 from sources 38. The relative thickness and composition of each of the plurality of predefined coatings 30 may individually or both continuously vary as the result of the thickness profile 48 (see Figs. 4-7) of each of the materials A and B as they are delivered to the substrate 18. This continuous variation may be linear or non-linear, depending on variables such as the delivery angle α, the projective power of the delivery mechanism 12 (not shown) associated with each source 38, the coating speed or amount of material deposited per unit time, the feed rate and concentration of the material input into the delivery mechanism, the vertical spacing 60, the offset distance 59 of the source 38 relative to the center point 44, the horizontal spacing 53 of each source 38 to the center point 44, the shape of the envelope 40 (not shown), the atmosphere and power per area and pressure and species of gas in vapor deposition, and other similar factors. Each of these variables may be varied individually or in combination to produce a predefined coating in each predefined region 30. Further, although not shown, a mask 32 may be positioned between each of the sources 38 and the substrate 18, preferably adjacent to or touching the substrate to assist in forming the coating library.

Additionally, referring to Fig. 8, the delivery angle α may have a value in the range of about 0° to about 90°, more preferably from about 15° to about 75°, and most preferably from about 30° to about 60°. The vertical spacing 60 may vary from about 0 cm to about 90 cm, more preferably from about 3 cm to about 30 cm, and most preferably from about 10 cm to about 20 cm. The horizontal spacing 53 may vary

from about 0 cm to about 60 cm, more preferably from about 3 cm to about 30 cm, and most preferably from about 10 cm to about 20 cm. The coating thickness may vary from about 1 nanometer to about 1 millimeter, more preferably from about 1 micrometer (or microns) to about 500 micron, and most preferably from about 5 microns to about 100 microns.

Referring to Fig. 9, one embodiment of the coating library 64 produced by the combinatorial coating system 62 (Fig. 8) includes opposing gradients of materials A and B, ranging continuously from about 100% to about 0% of material A and from about 0% to about 100% of material B moving laterally across the coating library from the side adjacent to the source 38 of material A. Depending on the variables discussed above with regard to the delivery of the materials to the substrate, the coating library 64 may have a substantially constant or a variable thickness across the substrate. Preferably, the sources of materials A and B have respective points of focus 42 having a predefined offset distance 53 from the center point 44 of the delivery area so that the thickness of the coating library is substantially constant across the substrate. Further, by allowing a sufficient time for diffusion of materials A and B by controlling the rate of evaporation, a new material may be formed by the in-situ diffusion/mixing or by the reaction of A and B. Alternatively, the substrate 18 of Fig. 8 may be movable, such as rotationally, longitudinally and laterally, to obtain multiple variations in the composition of each of the predefined coatings 30. Further, the sources 38 may be sequentially fed with new and different materials, which in combination with a laterally moving elongated substrate, results in a continuously varying coating along a longitudinal length of the substrate. Additionally, each source 38 preferably is positioned within a delivery plane 65 that is substantially parallel to, but spaced a vertical distance 60 from, the plane 49 of the delivery area. In an alternate embodiment, however, the vertical spacing 60 of each source 38 may independently vary to provide a different thickness profile 48 within the delivery area 24. Thus, the system 62 of provides for the simultaneous delivery of at least two of a plurality of materials onto the substrate to obtain a continuously varying coating having gradients of the at least two materials.

Referring to Figs. 10-11, in another embodiment similar to that of Figs. 8-9, a ternay combinatorial coating system 68 provides a continuous ternary coating library 70. At least three materials (A, B and C) of a plurality of materials 14 (Fig. 1) may be simultaneously or sequentially delivered from sources 38. The sources 38 are each positioned in a substantially identical angled off focus setup 61 (Fig. 7), as described above. The sources 38 are preferably equally spaced about a circle 74 having a center 76 on the same axis 78 as center point 44. Preferably, the circle 74 has a diameter larger than the diameter of the delivery area. For example, the circle 74 preferably has a diameter of about 30 cm while the delivery area has a diameter in the range of about 10 cm to about 15 cm. The coating library 70 formed by system 68 may be a continuously varying combination of each of the three materials A, B and C, mimicking a ternary phase diagram. The same variables affecting the formation of the coating library 64 (Figs. 8-9), described above, similarly apply to the coating library 70 of the system 68. For example, the relative composition of the coating library 70 at any point is a function of the horizontal spacing 53, offset distance 59, the delivery angle α, the shape of the envelope 40 of the spray of each material, the point of focus 42 of each source, etc. Further, the preferred spacing and angles are the same as those described above with reference to Figs. 8-9. In one working example, three airbrush guns were simultaneously focused to deliver a fine spray of three different materials to the substrate utilizing an angled, off-focus set up 61 (Fig. 7). All of the guns were positioned in a delivery plane parallel to and vertically spaced about 15 cm from the delivery area. Further, each gun was positioned to have a delivery angle α of about 45° and a horizontal spacing 53 of about 18 cm. The substrate 18 was a substantially circular disk of silicon wafer material having a diameter of about 8 cm. Each of the plurality of predefined regions were sized to form a coating library having 66 predefined coatings. The coating material included 2% polyethylmethal acrylate (PEMA) in iso-propanol solvent mixed with an organic pigment. After deposition through a ternary or triangle mask (not shown) and thermal curing, a ternary coating library having 66 distinct compositions was generated in a few minutes. The coating was about 2 microns in thickness, and the coating thickness scales linearly with the coating time.

Referring to Figs. 12-14, in another embodiment, a combinatorial coating system 72 includes a plurality of co-focused or simultaneously focused delivery mechanisms 12 each fixedly positioned to simultaneously or sequentially deliver one of the plurality of materials 14 to the substrate 18 through a mask 32. Each of the plurality of delivery mechanisms 12 produces a mist of atomized material within an envelope 40 (Fig. 3) that intersects with the surface 16 of the substrate 18. Each source 38 is preferably positioned in an angled, off-focus set up 61 (Fig. 7). Preferably, each delivery mechanism 12 is equally spaced about a circle 74 having a center 76 on the same axis 78 as center point 44. Further, each delivery mechanism 12 preferably has a horizontal spacing 53 (Fig. 7) radially from the center 76 a distance less than the distance from the center point 44 to the edge of the delivery area 24. Preferably, the point of focus 42 (not shown) of each delivery mechanism 12 is focused a substantially equivalent offset distance 59 (Fig. 7) from the center point 44, thereby positioning the same portion of the thickness profile 48 (Fig. 7) for each material in the delivery area 24. However, the point of focus 42 for each delivery mechanism 12 is not required to be offset from the center point 44 or to have equivalent offset distances 53. In fact, each delivery mechanism 12 may have a unique point of focus 42, including one that results in the centerline 46 (Fig. 3) being normal or angled relative to the surface 16 while the delivery mechanism is in line with or radially spaced away from the center point 44, as long as the envelope 40 (Fig. 3) of the delivered material 14 coincides with at least a portion of the delivery area 24, and hence the surface 16 of the substrate 18. Further, the delivery mechanisms 12 need not be positioned about a circle, but may be in any relative position that allows the parallel or simultaneous delivery of a plurality of materials 14 to at least a portion of the delivery area 24.

The mask 32 preferably comprises a plurality of patterns 80 (Fig. 13), which may be moved in and out of the line of delivery of the materials 14 in order to control the coating of different predefined regions 22 (Fig. 2) with different materials to form a coating library 82 (Fig. 13). Although depicted in Fig. 12 as being spaced apart from substrate 18, preferably the mask is a physical contact mask that is touching or in close proximity to the substrate to eliminate shadowing. For example, referring to

Fig. 14, the system 72 may produce a coating library 82 having sixteen predefined coatings 30 using four (A, B, C and D) of the plurality of materials 14 in combination with the first four patterns 80 of the mask 32 (Fig. 13).

In a working example of the system 72, each delivery mechanism 12 is a sprayer nozzle that atomizes a liquid precursor material 14 into a fine spray and directs it individually or in combination with other nozzles/materials to the substrate 18 to make a coating layer. Compressed air, superheated steam, or an ultrasonic wave may be applied to the liquid material to generate the fine mist of the liquid material. A coating library 82 having multiple coating layers may be developed by sequencing the delivery of the materials 14 from the plurality of sprayers 12 in combination with a sequence of masking patterns and curing steps (if necessary) to provide a predetermined coating 30 in a predefined region 22 (Fig. 2) of the substrate. This may be desirable, for instance, when searching for a coating having multi-functional properties where each one or a combination of the coating layers provides at least one of the functional properties. In this particular example, which should not be construed as limiting, eight different liquid coatings (A-H) are fed to eight individually controlled spray guns. For example, suitable liquid coating materials include polyacrylides, polycarbonates, vinyl polymer, silicones, and silica gel. Further, for example, suitable spray guns include those manufactured by SonoTech. If the materials require curing, then suitable examples of a curing source 34 (Fig. 1) include a hot plate and a UV lamp capable of curing the materials at temperatures of about 80 to about 200, and more preferably about 100 to about 150, for time periods of about 10 min to about 10 hours, and more preferably about 1 hour about 4 hours. Thus, a coating library having a plurality of predefined multi-layer coatings is made in a parallel fashion, either by combining different masking patterns with different liquid precursor materials, or by a maskless "continuous phase spreading" of the materials, taking advantage of the variation in spacing and volume of the liquid precursor material being delivered from each sprayer nozzle to form the coating library.

Referring to Fig. 15, in another embodiment, a vapor deposition combinatorial coating system 90 includes multiple delivery mechanisms 12 each co-focused, or

simultaneously focused, for simultaneously or sequentially delivering one of a plurality of solid materials 14 to the substrate 18 positioned on a movable stage 92 within a deposition housing 94. To withstand the high temperature of vapor deposition, the substrate comprises a stable high temperature material such as magnesium oxide or lanthanum aluminate ($LaAlO_3$). The deposition housing 94 is sealable to form a vacuum chamber 96 within its interior surfaces. In this case, the delivery mechanisms 12 are vapor deposition devices, such as sputter guns powered by RF power, preferably matched for optimum output. The stage 92 supports the substrate 18 in a known position, where the stage may adjust vertically, rotationally or linearly to position the substrate within the delivery area. Positioned between the delivery mechanisms 12 and the substrate 18 is a mask 32 having an array of different patterns 80. The mask 32 is preferably substantially in contact with the substrate 18 during vapor deposition, to minimize the "shadowing effect." The mask 32 is movably positioned within a vacuum chamber 98 of a mask housing 100. The mask housing 100 is in communication with the main housing 94 in a manner to maintain the atmosphere of both vacuum chambers 96 and 98. Further, the mask housing 100 includes a gear box 102 and micrometer 104 for moving and measuring, respectively, the position of the mask patterns 80 with respect to the substrate 18.

Further, the system 90 may optionally may include a shutter 106 having one or more apertures 108 to select one or more materials for simultaneous or sequential delivery and prevent intermixing of materials. The shutter 106 is movably connected to a rotor 110 that rotates the shutter and aperture 108 to select the solid material 14 to vaporize, while the mask pattern 80 is changed in-vacu with linear motion vacuum feed-through. The quantity of deposition of the materials 14 is monitored with a thickness monitoring device 112, such as a quartz crystal oscillator. By vapor deposition of different solid precursors through different patterns of masks, a substrate with more than 100 different coating composition/layer structures can be fabricated in a day without need to break vacuum to change solid materials and/or mask patterns.

The vacuum atmosphere within the vacuum chambers 96 and 98 are maintained by a back-pump station 114 connected to a turbo-molecular pump 116.

For example, the back-pump station 114 may provide a vacuum of about 10^{-3} torr, while the turbo-molecular pump 116may provide a vacuum of 10^{-6} torr. The pumps 114 and 116 are in communication with the vacuum chamber 96 through a gate valve 118.

For example, this system 90 may generate coating libraries of any ceramic, metallic and/or semiconductor materials, with surface roughness and accuracy of thickness measured in nanometers. Besides the sputter devices described above, other suitable delivery mechanisms 12 include laser ablation, electron beam evaporation, CVD, etc., that may be used with the masking system to generate inorganic coating libraries. To fabricate an organic coating library, a co-focusing multiple source thermal evaporation apparatus coupled with a masking system may be set up. The same system may be utilized to fabricate small molecule libraries such as for use in organic light emitting diode ("LED") devices.

It is apparent that there has been provided in accordance with this invention, a combinatorial coating system and method. While the invention has been particularly shown and described in conjunction with preferred embodiments thereof, it will be appreciated that variations and modifications can be effected by a person of ordinary skill in the art without departing from the scope of the invention. Further, it is to be understood that the principles of the positioning of the delivery mechanisms and the delivery of the materials to form the coating thickness profiles described herein apply in a similar manner, where applicable, to all embodiments.

WHAT IS CLAIMED IS:

1. A system (10) for making an array of coated materials, comprising:

a substrate (18) having a surface (16) with a plurality of predefined regions (22);

a plurality of materials (14) for coating the substrate;

a delivery mechanism (12) associated with the plurality of materials, wherein the delivery mechanism is positioned to simultaneously deliver each of the plurality of materials onto the surface of the substrate; and

a controller (26) that controls the delivery mechanism to selectively deliver each of the plurality of materials such that each of the plurality of predefined regions of the substrate has a predefined coating (30).

2. The system of claim 1, the delivery mechanism further comprising a plurality of sources (38), each of the sources for delivering one of the plurality of materials, wherein each of the plurality of sources has a different fixed positioned within the system.

3. The system of claim 1, wherein the predefined coating associated with at least one of the plurality of regions comprises a thin film coating having multiple layers.

4. The system of claim 1, further comprising a mask (32) having a plurality of patterns, the mask positioned adjacent to the surface of the substrate, wherein each of the plurality of patterns is positionable over the substrate, and wherein each of the plurality of patterns is unique to permit delivery of the materials to different combinations of the plurality of predefined regions of the substrate.

5. The system of claim 1, wherein each of the plurality of materials comprises a material selected from the group consisting of metals, alloys, ceramics, oxides, nitrides and sulfides.

6. The system of claim 1, wherein each of the plurality of materials comprises a material selected from the group consisting of polymeric materials, oligomeric materials, small molecules, thermoplastic polymers and thermosetting polymers.

7. The system of claim 1, wherein the delivery mechanism further comprises a vapor deposition device.

8. The system of claim 7, wherein the delivery mechanism further comprises:

a shutter having a plurality of positions corresponding to each of the plurality of materials, wherein the controller controls the position of the shutter to selectively expose at least one of the plurality of materials to the surface of the substrate.

9. The system of claim 1, wherein the delivery mechanism further comprises:

a plurality of sprayer devices corresponding to the plurality of materials, wherein each of the plurality of materials is vaporizable by the corresponding one of the plurality of sprayer devices.

10. The system of claim 1, further comprising:

a mask having a plurality of masking patterns; and

a movable mounting device (35) in communication with the controller and having a mount for holding the mask, wherein the controller controls movement of the mounting device to position one of the plurality of masking patterns over the substrate in conjunction with the delivery of at least one of the plurality of materials to the substrate.

11. The system of claim 1, further comprising a movable holding device (37) in communication with the controller and having a fixture for supporting the substrate, wherein the controller controls the speed of movement of the supporting device to position at least a portion of the substrate in a delivery area for receiving the delivery of at least one of the plurality of materials.

12. The system of claim 11, wherein the holding device is movable at a substantially constant rate.

13. A system (10) for making an array of coated materials, comprising:

a delivery area (24) fixedly positioned within the system;

a substrate (18) having a surface (16) with a plurality of predefined regions (22), the surface of the substrate positionable within the delivery area;

a plurality of materials (14) for coating the substrate;

a delivery mechanism (12) associated with the plurality of materials, wherein the delivery mechanism is positioned to simultaneously delivery each of the plurality of materials from a different fixed position into the delivery area; and

a controller (26) that controls the delivery mechanism to selectively deliver at least one of the plurality of materials to the delivery area such that each of the

plurality of predefined regions of the substrate has a predefined coating (30) of at least one of the plurality of materials.

14. The system of claim 13, wherein the predefined coating associated with at least one of the plurality of regions comprises a thin film coating having multiple layers.

15. The system of claim 13, further comprising a mask having a plurality of patterns, the mask positioned adjacent to the delivery area between the plurality of materials and the surface of the substrate, wherein each of the plurality of patterns is positionable within the delivery area, and wherein each of the plurality of patterns is unique to permit delivery of the materials to different combinations of the plurality of predefined regions of the substrate.

16. The system of claim 13, wherein each of the plurality of materials comprises a material selected from the group consisting of metals, alloys, ceramics, oxides, nitrides and sulfides.

17. The system of claim 16, wherein the delivery mechanism further comprises a vapor deposition device.

18. The system of claim 17, wherein the delivery mechanism further comprises:

a shutter having a plurality of positions corresponding to each of the plurality of materials, wherein the controller controls the position of the shutter to selectively expose at least one of the plurality of materials to the delivery area.

19. The system of claim 13, wherein each of the plurality of materials comprises a material selected from the group consisting of polymeric materials, oligomeric materials, small molecules, thermoplastic polymers and thermosetting polymers.

20. The system of claim 19, wherein the delivery mechanism further comprises:

a plurality of sprayer devices corresponding to the plurality of materials, wherein each of the plurality of materials is vaporizable by the corresponding one of the plurality of sprayer devices.

21. The system of claim 13, further comprising a movable mounting device (35) in communication with the controller and having a mount for holding the mask,

wherein the controller controls movement of the mounting device to position one of the plurality of patterns over the delivery area in conjunction with the delivery of at least one of the plurality of materials to the delivery area.

22. The system of claim 21, further comprising a movable holding device (37) in communication with the controller and having a fixture for supporting the substrate, wherein the controller controls the speed of movement of the supporting device to position at least a portion of the substrate within the delivery area in conjunction with the delivery of at least one of the plurality of materials to the delivery area.

23. The system of claim 22, wherein the holding device is movable at a substantially constant rate.

24. A method for making an array of coated materials, comprising:

providing a substrate (18) having a surface (16) with a plurality of predefined regions (22); and

selectively delivering at least one of a plurality of materials (14) to the surface of the substrate to form a predefined coating (30) on each of the plurality of predefined regions of the substrate, where each of the plurality of materials is positioned for simultaneous delivery to the substrate.

25. The method of claim 24, wherein selectively delivering at least one of the plurality of materials further comprises delivering each of the plurality of materials from a different fixed position.

26. The method of claim 24, wherein the predefined coating comprises a thin film coating.

27. The method of claim 24, wherein the predefined coating comprises a thin film coating having multiple layers.

28. The method of claim 24, further comprising positioning a mask (32) between the surface of the substrate and the at least one delivered material.

29. The method of claim 28, where positioning the mask further comprises selectively positioning one of a plurality of mask patterns between the surface of the substrate and the at least one delivered material.

30. The method of claim 24, where each of the plurality of materials comprises a material selected from the group consisting of metals, alloys, ceramics, oxides, nitrides and sulfides.

31. The method of claim 24, where each of the plurality of materials comprises a material selected from the group consisting of polymeric materials, oligomeric materials, small molecules, thermoplastic polymers and thermosetting polymers.

32. The method of claim 24, where selectively delivering at least one of the plurality of materials further comprises vaporizing the material.

33. The method of claim 24, where selectively delivering at least one of the plurality of materials further comprises positioning an aperture in a shutter between the selected material and the substrate.

34. The method of claim 24, further comprising moving the substrate during the delivery of the at least one of the plurality of materials to the substrate.

35. The method of claim 24, further comprising positioning one of a plurality of patterns of a mask between the selected material and the substrate.

36. A method for making an array of coated materials, comprising:

positioning a substrate (18) having a surface (16) with a plurality of predefined regions (22) such that the surface of the substrate is within a delivery area (24), where the delivery area is fixedly positioned; and

selectively delivering at least one of a plurality of materials (14), each from a different fixed position, to the delivery area to form a predefined coating (30) of at least one of the plurality of materials on each of the plurality of predefined regions of the substrate.

37. The method of claim 36, wherein the predefined coating comprises a thin film coating.

38. The method of claim 36, wherein the predefined coating comprises a thin film coating having multiple layers.

39. The method of claim 36, further comprising positioning a mask (32) between the surface of the substrate and the at least one delivered material.

40. The method of claim 39, where positioning the mask further comprises selectively positioning one of a plurality of mask patterns between the surface of the substrate and the at least one delivered material.

41. The method of claim 36, where each of the plurality of materials comprises a material selected from the group consisting of metals, alloys, ceramics, oxides, nitrides and sulfides.

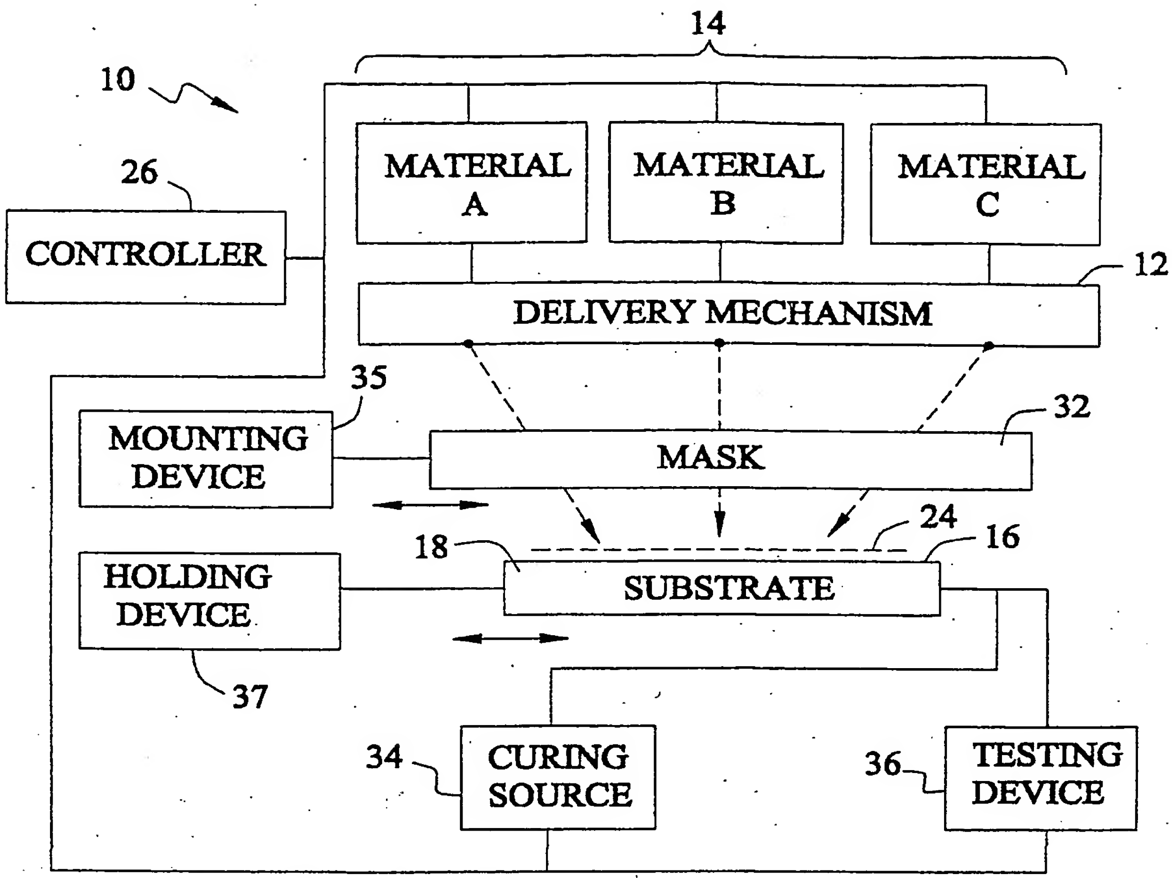
42. The method of claim 36, where each of the plurality of materials comprises a material selected from the group consisting of polymeric materials, oligomeric materials, small molecules, thermoplastic polymers and thermosetting polymers.

43. The method of claim 36, where selectively delivering at least one of the plurality of materials further comprises vaporizing the material.

44. The method of claim 36, where selectively delivering at least one of the plurality of materials further comprises positioning an aperture in a shutter between the selected material and the substrate.

45. The method of claim 36, further comprising moving the substrate during the delivery of the at least one of the plurality of materials to the substrate.

46. The method of claim 45, further comprising positioning one of a plurality of patterns of a mask between the selected material and the substrate.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10
26
MATERIAL A
MATERIAL B
MATERIAL C
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12
DELIVERY MECHANISM
35
32
MOUNTING DEVICE
MASK
24
18
16
HOLDING DEVICE
SUBSTRATE
37
34
CURING SOURCE
36
TESTING DEVICE

FIG. 1

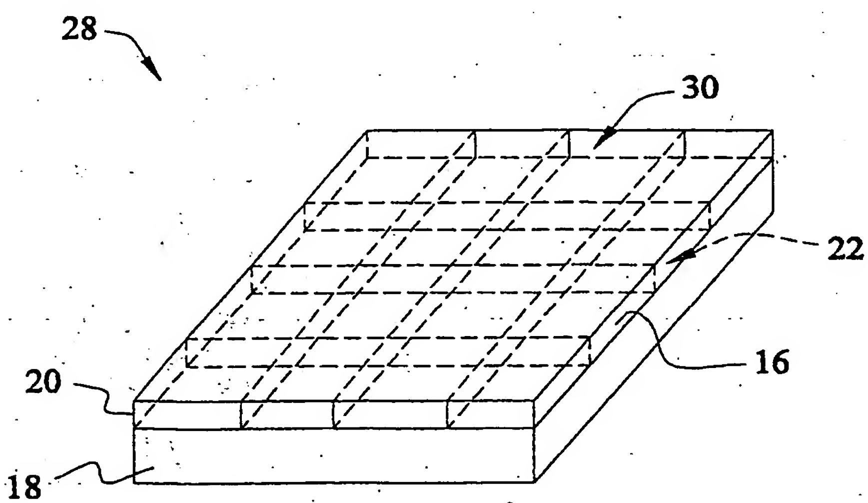
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FIG. 2

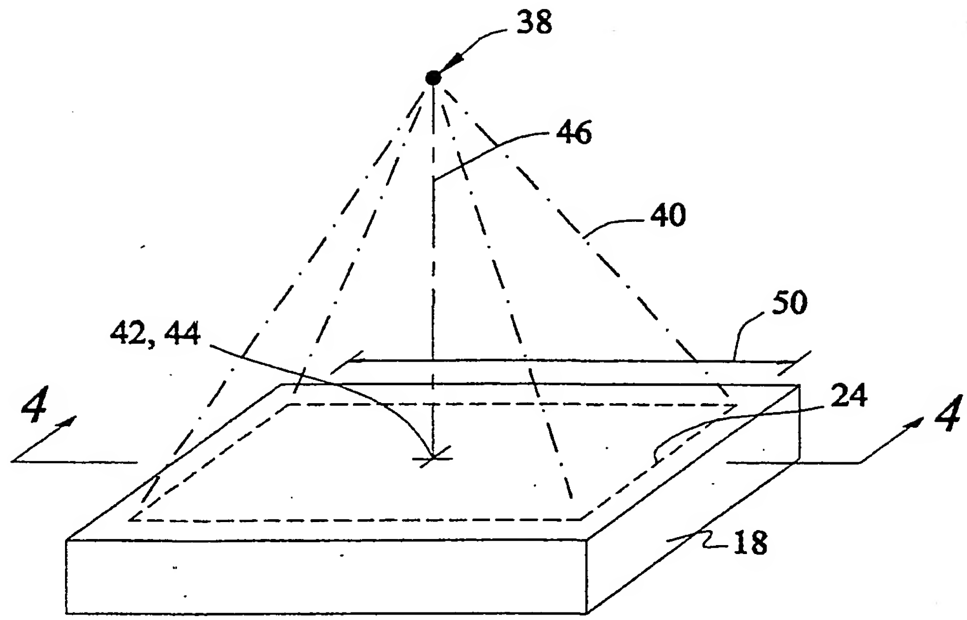


FIG. 3

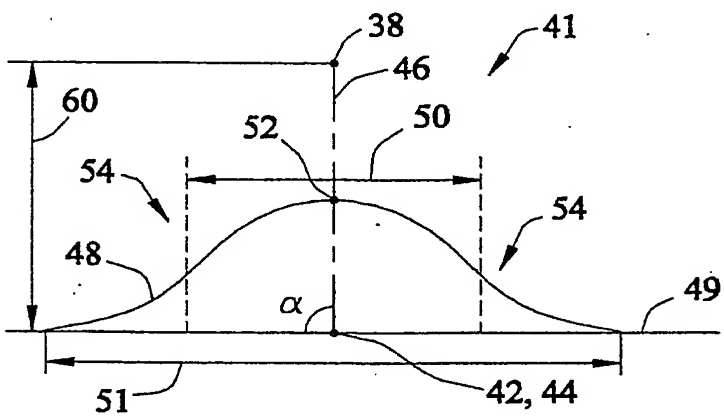


FIG. 4

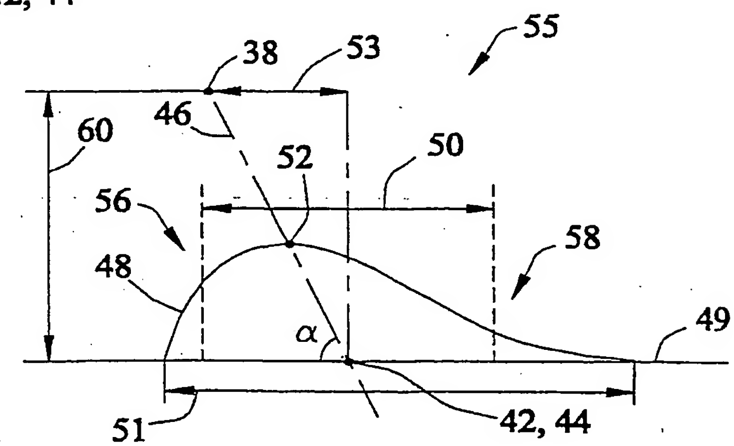


FIG. 5

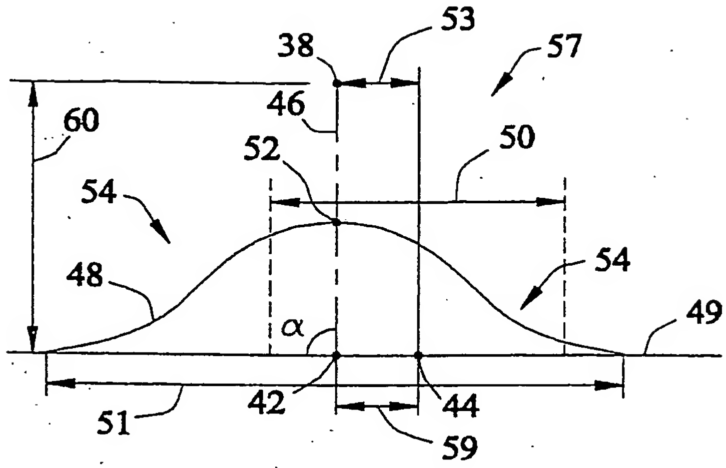


FIG. 6

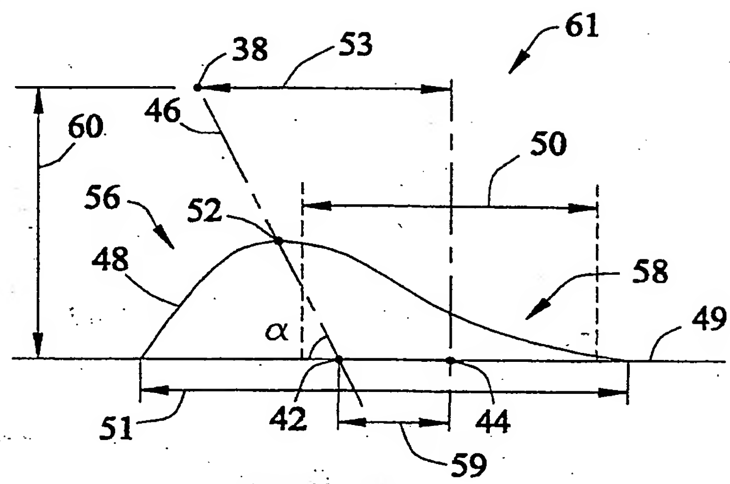


FIG. 7

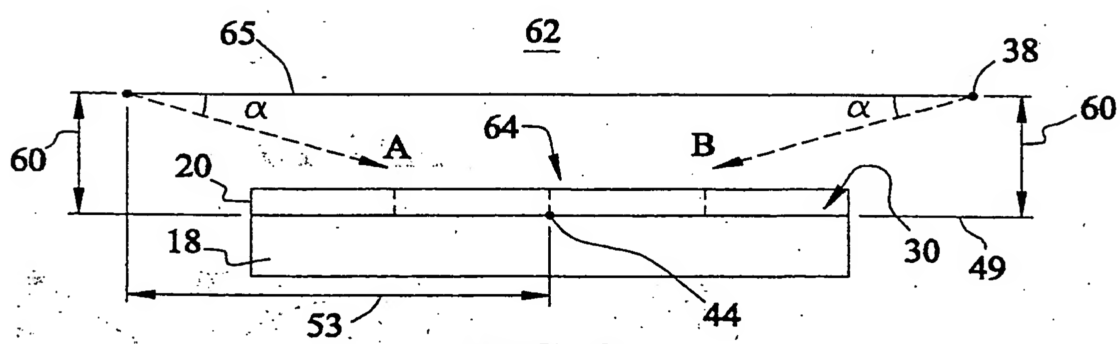


FIG. 8

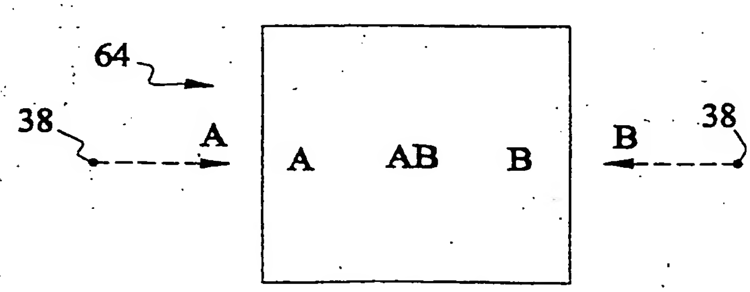
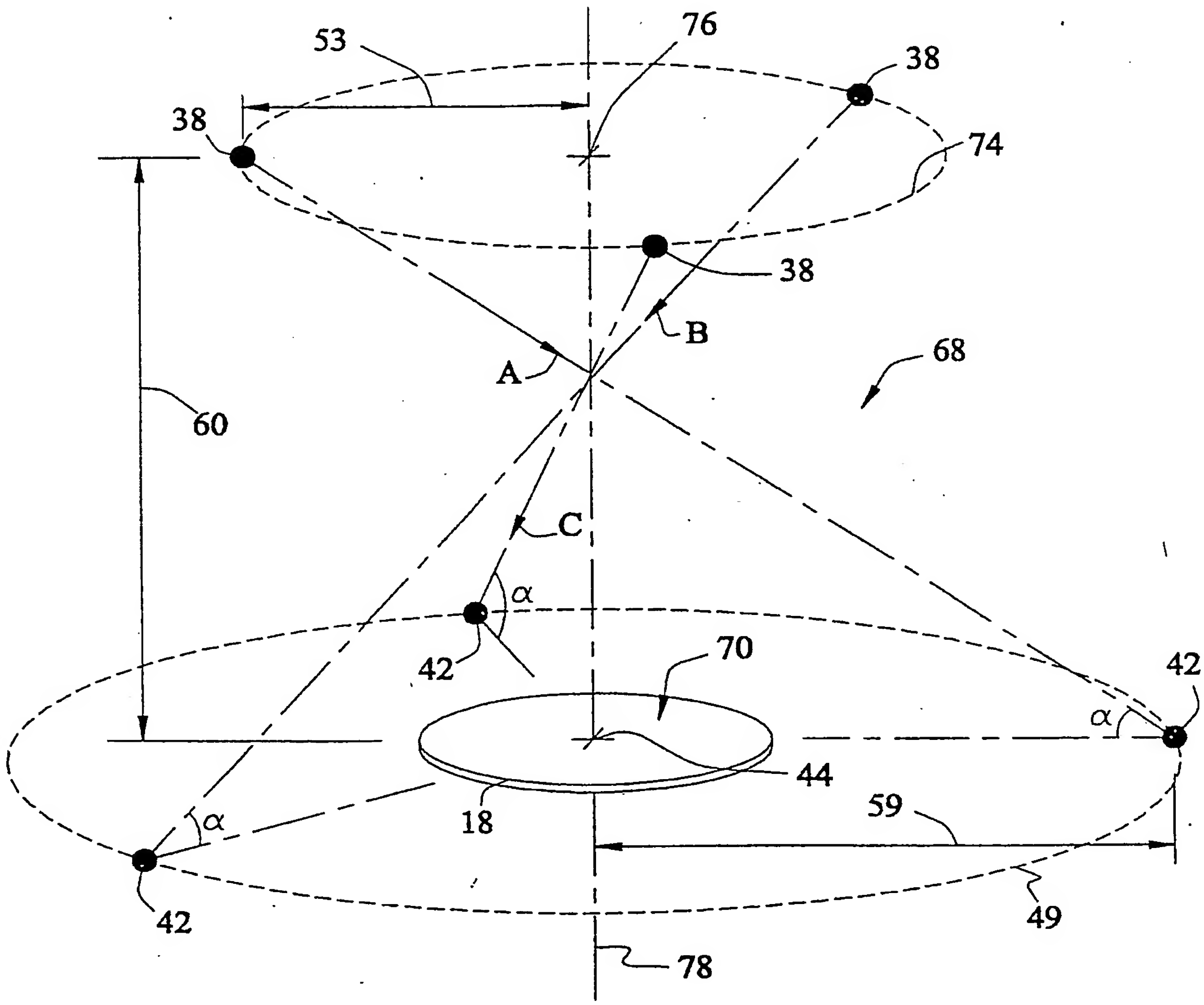


FIG. 9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53
38
38
74
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C
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α
44
α
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59
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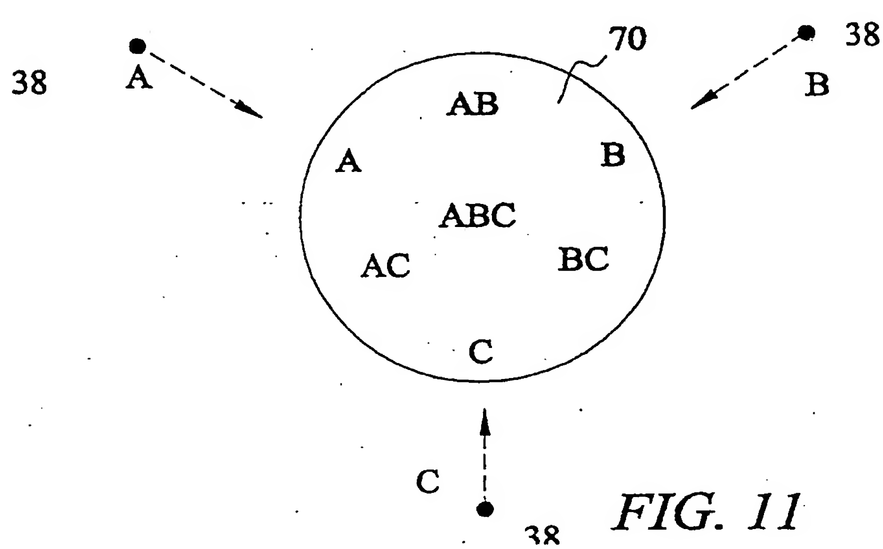
49
78

FIG. 10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C
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FIG. 11

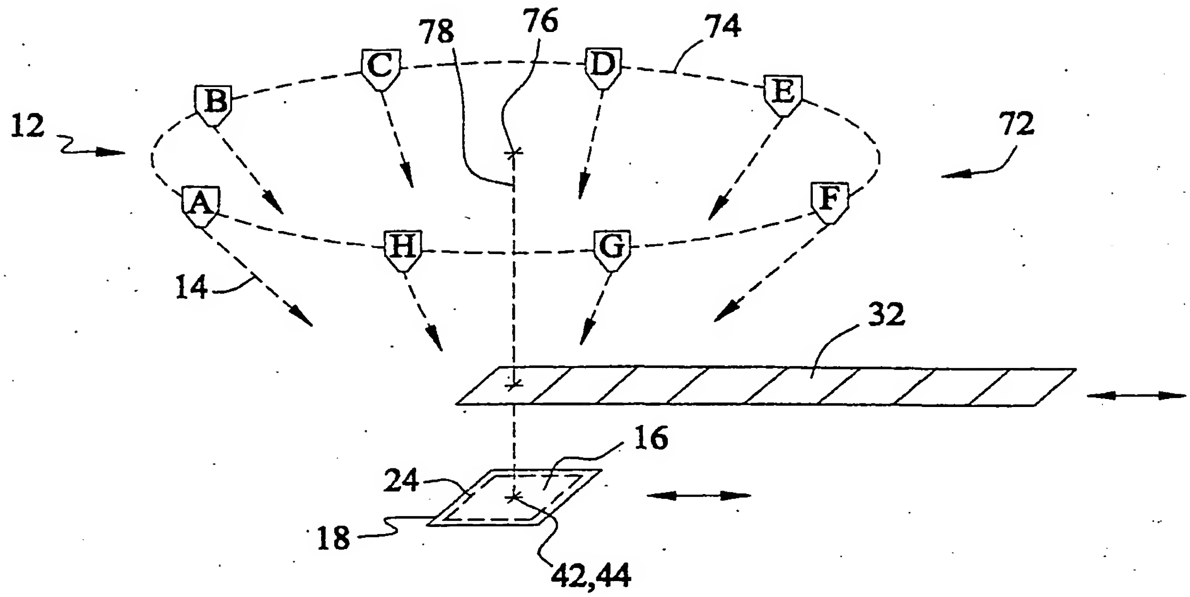

FIG. 12

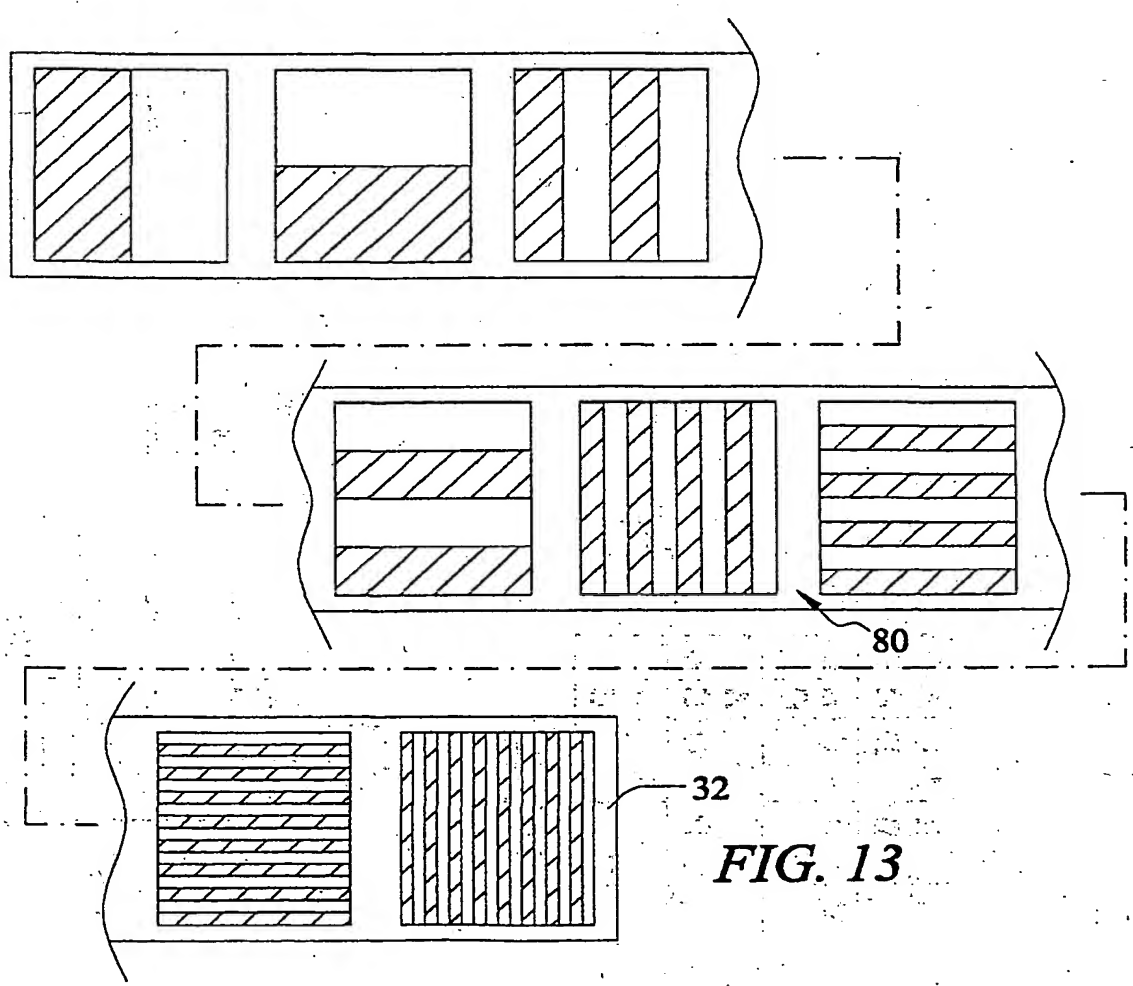

FIG. 13

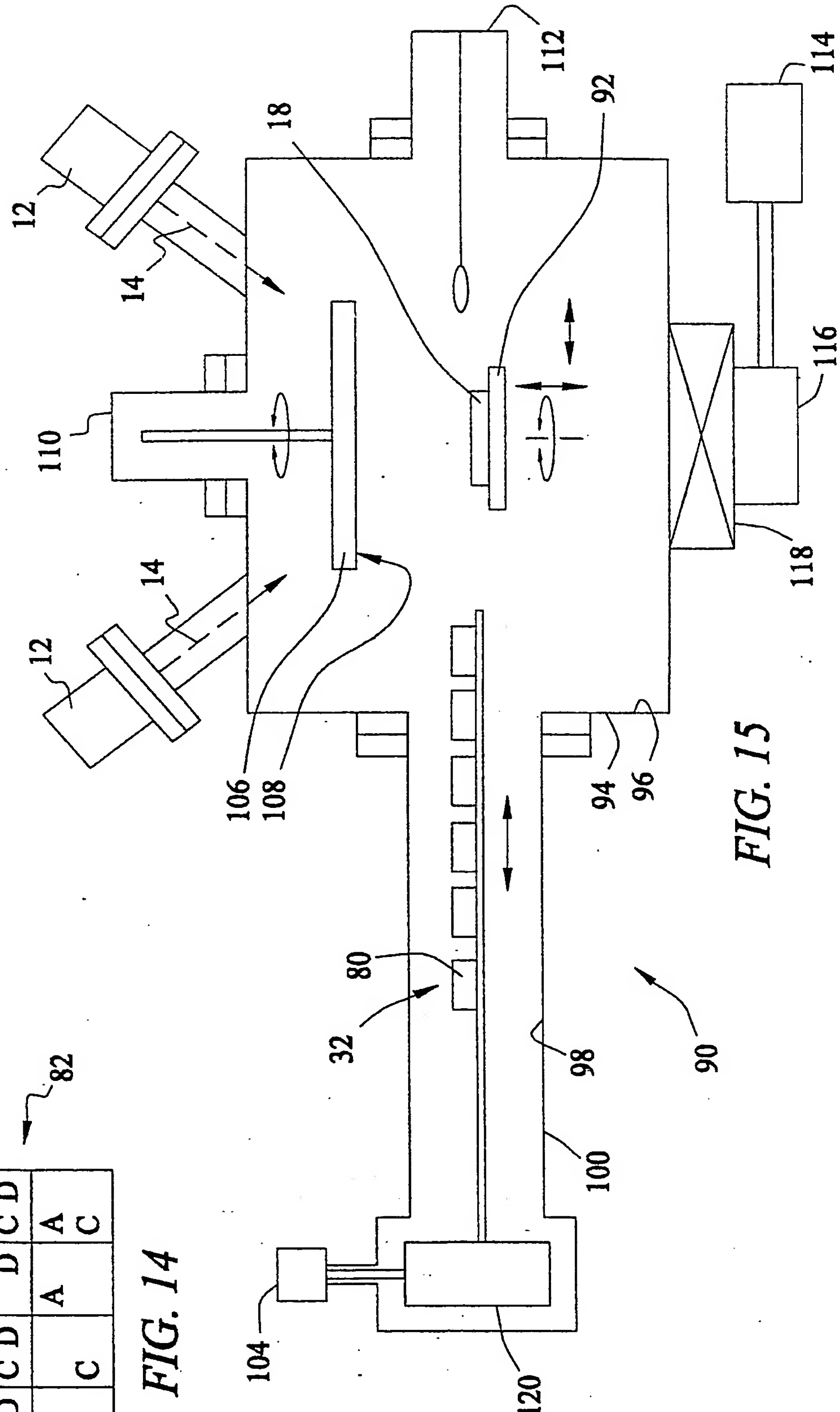
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FIG. 15

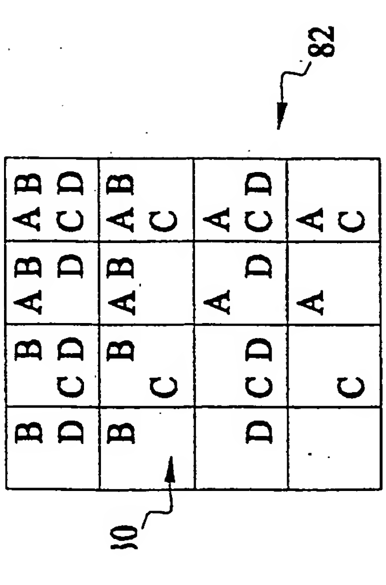
82
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FIG. 14

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/US 01/19159

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01J19/00 C23C14/00 C23C14/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01J C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 47613 A (SYMYX TECHNOLOGIES INC) 29 October 1998 (1998-10-29) page 1, line 29 -page 2, line 2 page 14, line 28 -page 15, line 9 page 16, line 3 - line 17 page 17, line 16 -page 18, line 7 page 23, line 4 -page 38, line 31; figures 5-14	1-46
X	WO 00 43119 A (WU XIN DI ;WANG YOUQI (US); SYMYX TECHNOLOGIES INC (US)) 27 July 2000 (2000-07-27) page 5, line 22 -page 12, line 12; claims 1-16; figures 1-8	1-3,5-9, 13,14, 16-20, 24-28, 30-32, 36-39, 41-43

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
5 February 2002	13/02/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Veefkind, V

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/19159

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 01 85364 A (INTEMATIX CORP) 15 November 2001 (2001-11-15) abstract; claims 1-36; figures 1-15	1,13,24, 36

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 01/19159

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
WO 9847613	A	29-10-1998	US	6045671	A	04-04-2000
			EP	0917494	A1	26-05-1999
			JP	2000503753	T	28-03-2000
			WO	9847613	A1	29-10-1998
WO 0043119	A	27-07-2000	AU	2632800	A	07-08-2000
			WO	0043119	A1	27-07-2000
WO 0185364	A	15-11-2001	WO	0185364	A1	15-11-2001